NASA TT F-9875

SELECTION OF THE CONDITIONS OF CHROMATOGRAPHIC ANALYSIS OF GAS MIXTURES CONTAINING CO_2, C_nH_m, O_2, H_2, N_2, CO, CH_4, C_2H_6

N.S.Torocheshnikov, V.A.Semenova, and G.A.Gerasimova

Translation of "O vybore usloviy khromatograficheskogo analiza gazovykh smesey, soderzhashchikh CO_2, C_nH_m, O_2, H_2, N_2, CO, CH_4, C_2H_6".
Zhurnal Prikladnoy Khimii, Vol.38, No.9, pp.2017-2026, 1965.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON
JANUARY 1966

SELECTION OF THE CONDITIONS OF CHROMATOGRAPHIC ANALYSIS OF GAS MIXTURES CONTAINING CO_2, C_nH_m, O_2, H_2, N_2, CO, CH_4, C_2H_6

N.S.Torocheshnikov, V.A.Semenova, and G.A.Gerasimova

A gas chromatographic apparatus, based on the principle of adsorbing a gas mixture on activated charcoal in the column and developing it in a carbon-dioxide stream, is described in detail with schematic diagram and discussion of physical bases. Tabulated data for various gas mixtures (H_2, N_2, CH_4, etc.) are given to show that efficiency of separation increases with column length. The time interval of separation of hydrogen and nitrogen was 30 sec in columns of 3.5 - 4 m length; nitrogen and carbon monoxide separated best in columns of 9 m length. U-shaped columns were easier to use but required more active carbon than spiral columns. Optimum flow rates of the carrier gas are calculated for maximum separation in minimum time.

Author

Recently many plants and research laboratories have been successfully using chromatographic analyses of mixtures containing H_2, N_2, CO, CH_4 and other gases.

It is known from literature sources (Bibl.1 - 3) that the efficiency of chromatographic analysis depends on the length and type of the adsorption layer (length of the chromatographic column), on the nature and size of the adsorbent grains, on the temperature and velocity of the carrier, on the volume of the gas sample, and on other analytical conditions.

---

* Numbers in the margin indicate pagination in the original foreign text.

To elicit the effect of various factors on the efficiency of chromatographic analysis of a mixture of H_2, N_2, CO, CH_4, and other components developed by carbon dioxide, we carried out a number of corresponding investigations. The experiments were made with the apparatus shown in Fig.1. We used the following method: acidic gases (CO_2, SO_2, H_2S, and others), unsaturated hydrocarbons, and oxygen were determined in accordance with the All-Union State Standard, just as on the VTI apparatus. Hydrogen, nitrogen, carbon monoxide, and methane were determined by chromatographic analysis in the following manner: During the absorption analysis the chromatographic part of the apparatus was filled with carbon dioxide and checked for airtightness; the carbon dioxide flow rate, used in the analysis, was then established.

At the end of the absorption analysis (after determining the oxygen), a sample was selected for chromatographic analysis. Before sampling, the stopcocks on the absorption vessels 1-4 are set to connect the buret 5 with the calibrated stopcock 6, and the equalizing flask 7 is set in the upper ring 8. A meniscus of alkali is established at the top 9 of the measuring part of the /2018 buret. During sampling, the supply of carbon dioxide to the chromatographic column is stopped by discharging it into the atmosphere through the stopcock 10. To prevent the alkali from being sucked into the chromatographic column, the stopcock 11 is set in a neutral position so that, when turning it, the column does not communicate with the atmosphere. Then, the stopcock 6 is turned to communicate with the atmosphere and about 20 ml of gas, left in the buret 5 after the absorption analysis, is allowed to pass through it. After this, the stopcock 6 is again turned to communicate with the chromatographic column. In this manner, the coil of the stopcock 6 is filled with the test gas, i.e., a gas sample is taken for chromatographic analysis. After sampling, the stopcock 11

is turned to connect the chromatographic column with the buret 9 and, by a corresponding turn of the stopcock 10, the flow of carbon dioxide is again directed into the chromatographic column. When gas bubbles appear in the buret 9, a stopwatch is started and this instant is considered the start of analysis.

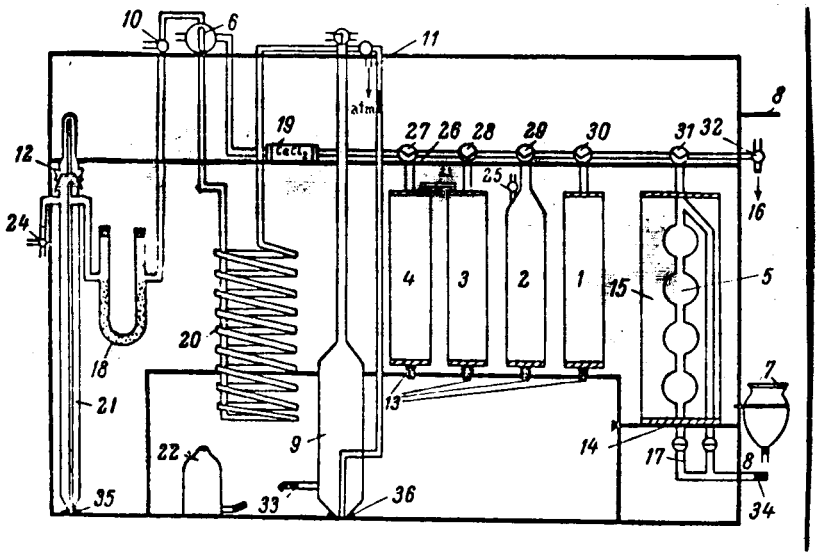

Fig.1 Schematic Diagram of Chromatograph
1-4) Absorption vessel; 5) Buret for measuring gas volume; 6) Four-way stopcock for intake of sample; 7) Equalizing flask to buret 5; 8) Metal rings with groove and rubber gasket for equalizing flask; 9) Measuring-absorption buret; 10, 11, 24, 27-32) Crescent-shaped three-way stopcock; 12) Wooden frame for attaching parts of instrument and for use as casing when transporting and storing the instrument; 13) Metal supports for installing absorption vessels; 14) Metal support for installing buret; 15) Glass cylinder for equalizing and stabilizing the temperature of the buret; 16) Stopper for closing the free capillaries of the stopcock branches; 17) Forked T-piece with two direct stopcocks to buret 5; 18, 19) Calcium chloride tubes; 20) Absorption column, 4.5 mm long and 4.5 - 5 mm in diameter; 21) Flow meter; 22) Equalizing flask to measuring-absorption buret; 23) Isolating branched tube connected with hydraulic gate or with rubber bag; 25) Safety pipe with spherical expansion; 26) Strip for attaching stopcocks; 23, 24) Rubber tubes; 35, 36) Recesses for attaching buret and flow meter.

The principle of the analysis consists in feeding the gas mixture to the chromatographic column with activated charcoal and developing it by a stream of carbon dioxide.

As a result of continuous adsorption and desorption, the components of the gas mixture are separated on passing through the column, so that between the separation of individual components there are time intervals in which only the developer is separated.

The gas stream from the chromatographic column (during analysis) enters the measuring-absorption buret 9 which contains a solution of alkali. Here, /2019 the carbon dioxide is absorbed and the components being determined are collected in turn in the buret 9 where their volumes are measured. During the analysis, we recorded the level of the alkali in the buret 9 and the time corresponding to it at the start of the analysis and at the end of separation of each component. Furthermore, to calculate the time interval between separation of the components, we recorded the time of the start of separation of each component in certain analyses. After completing the analysis, the next analysis can begin immediately. Between analyses the chromatograph is continuously blown with carbon dioxide, which is discharged into the atmosphere through the stopcock 11.

The percentage of the components was calculated by the following formula:

$$x = \frac{(v_e - v_s) - K(t_e - t_s)}{W} \cdot C\%,$$

where v_e, v_s are the gas volumes in the measuring-absorption buret corresponding to the end and start of separation of the component under consideration, reduced to atmospheric pressure (ml); K is the "blank"* (ml/min); C is the residue of the gas sample after absorption analysis (%); W is the volume of the gas sample taken for chromatographic analysis (ml) calculated by the formula

$$W = V_e - V_0 - t_{total} \cdot K,$$

* "Blank" - the magnitude characterizing the quantity of admixtures separated from carbon dioxide per minute in one milliliter.

where V_e, V_0 are the gas volumes at the end and start of analysis reduced to atmospheric pressure (ml); t_{tot} is the duration of chromatographic analysis equal to the end of separation of the last component (min). In conducting the analysis, it is necessary to take into account the following:

1) The start of the analysis is taken as the start of separation of hydrogen, in the calculation. The time and reading of the buret at the end of separation of the preceding component, corresponding to this time, is taken as the start of separation of subsequent components.

2) In the calculation, for the end of separation of a component we can take the readings of the buret and the corresponding time not strictly at the end of separation of the component, but at any subsequent instant before the start of separation of the next component (to simplify the calculation, it is convenient to take whole minutes), i.e., as long as the change in level in the buret 9 corresponds to the "blank".

To avoid errors in determining the end of separation of the components, two to three readings of the buret are taken every 10 - 20 sec at this time. For all practical purposes there will be no change in level in the buret within 10 - 20 sec, since the "blank" has an order of change in level of 0.01 ml/min.

3) The buret readings substituted into the calculation formula should be reduced to atmospheric pressure.

4) The connecting tubes in the chromatographic part of the apparatus should be capillary tubes. Wide connecting tubes cannot be used since the accuracy of analysis is reduced, owing to diffusion mixing.

5) The efficiency of the analysis is affected by the resistance of the columns, connecting tubes, and stopcocks. This resistance in all analyses should be the same, since the duration of analysis changes with a change of resistance.

The constancy of resistance is controlled in the following manner: upon switching the gas stream, by means of the stopcock 10, from the atmosphere to the chromatographic column, the reading of the flow meter (resistance) should change by a similar value (by not more than 20 mm H_2O).

In working out the method of chromatographic analysis of a mixture of /2020 H_2, N_2, CO, CH_4, we made a preliminary series of investigations on a spiral column of length ℓ = 1.5 m and diameter d = 8 mm, filled alternately with different grades of activated carbon (AG-2, AG-3, SKT, KAD) of different grain size, which were subjected to various heat treatments. Since good results were obtained when working with activated carbon AG-2, roasted for 15 min at a temperature of about 600°, with a grain size of 0.5 - 1 mm, most investigations devoted to a study of the effect of different factors on chromatographic analysis were performed on columns filled with this type of activated carbon.

In our investigations we studied the effect of: 1) length and shape of column, 2) flow rate of developer, 3) volume of sample.

Effect of length and shape of column on chromatographic analysis of H_2, N_2, CO, and CH_4. It is known from the literature (Bibl.4) that, with the same quantity of adsorbent, the separation of components improves with an increase in the length of the layer. Therefore when perfecting the method to improve the separation of H_2 and N_2 in the mixture of H_2, N_2 and CH_4, the analyses were carried out with approximately the same quantity of carbon (about 25 gm) in U-shaped columns (ℓ = 1 m, d = 10 mm) and in spiral columns (ℓ = 1.5 m, d = 8 mm; ℓ = = 2 m, d = 7 mm; ℓ = 3.5 m, d - 5.5 mm; ℓ = 4.5 m, d = 4.5 mm).

Most analyses were made on mixtures of high hydrogen concentration.

In performing mass analyses by using the first variants of the method (Bibl.5 - 8) it was found that N_2 and CH_4 are satisfactorily separated no matter

what their concentration in the gas mixture, whereas hydrogen and nitrogen in certain analyses at high hydrogen concentrations either do not separate at all or, if they do separate, the time intervals between the separation of components are extremely short, which interferes with the buret readings at the end of hydrogen separation. In our experiments, we attempted to define the optimum conditions for satisfactory separation of nitrogen and hydrogen at high concentration.

The results of the analyses (average of 3 - 4 analyses) in columns of various length, for a sample volume of about 4 ml at a carbon dioxide delivery rate of about 20 ml, are shown in Table 1.

In each analysis we determined: the time interval between separation of two adjacent components h (time between the end of separation of the preceding component t_e, and the start of separation of the subsequent component t_s), width of the bands $\Delta t = \mu$ (duration of discharge of the components from the chromatographic column), total duration of analysis t_{tot}, and percentage of components.

It is apparent from the data of Table 1 that separation in columns of different lengths, at the same quantity of adsorbent, is different even for gas mixtures close in percentage composition.

Efficiency of separation increases with an increase in column length: With columns of 1 m, 1.5 m, and 2 m in length, the time intervals between separation of hydrogen and nitrogen (at their high percentage content) are small or absent altogether. An analysis with a 4-ml sample cannot be performed on these columns since it is difficult to note the end of hydrogen separation. Good results were obtained with columns of 3.5 and 4.5 m length. The time intervals between separation of hydrogen and nitrogen in these columns were more than 30 sec.

Our studies involved hundreds of analyses of gas mixtures of H_2, N_2, and

CH_4 with different concentrations, using columns of about 4 m length and 4.5 - 5 mm diameter. The discrepancies in these analyses did not exceed 0.2 abs%.

We were able to work with the same adsorbent for several months, without regeneration.

TABLE 1 /2021

RESULTS OF INVESTIGATING THE CHROMATOGRAPHIC SEPARATION OF GAS MIXTURES OF H_2, N_2, AND CH_4 IN COLUMNS OF DIFFERENT LENGTH, WITH THE SAME QUANTITY OF ADSORBENT

Column Length (m)	Component	μ	h	t_{total}	Component Content %
1	H_2	6 min 20 sec	Did not separate	14 min	33.2
	N_2	H_2 and N_2			38.4
	CH_4	8 min 40 sec	8 min		28.4
1.5	H_2	3 min			33.0
	N_2	3 min 10 sec	0 min 10 sec	14 min 30 sec	38.4
	CH_4	3 min 10 sec	3 min 20 sec		28.6
2	H_2	3 min 50 sec			36.1
	N_2	2 min 50 sec	0 min 20 sec	16 min 40 sec	37.7
	CH_4	5 min	4 min		26.2
2	H_2	4 min 20 sec			65.0
	N_2	2 min 40 sec	0 min 10 sec	15 min 20 sec	33.0
	CH_4	2 min 20 sec	3 min		2.0
3.5	H_2	4 min 40 sec			41.9
	N_2	2 min 30 sec	1 min	18 min	10.9
	CH_4	3 min 20 sec	6 min		47.2
3.5	H_2	6 min			76.4
	N_2	3 min	0 min 30 sec	17 min	19.3
	CH_4	2 min	4 min		4.3
4.5	H_2	3 min 30 sec			49.9
	N_2	2 min 30 sec	1 min 30 sec	18 min 10 sec	18.1
	CH_4	3 min 50 sec	5 min 30 sec		32.0
4.5	H_2	5 min 10 sec			72.3
	N_2	2 min 30 sec	0 min 50 sec	17 min	14.8
	CH_4	3 min 20 sec	6 min		12.9

Using spiral columns from 4.5 to 15 m in length with a diameter of 4.5 mm, containing different quantities of activated carbon AG-2 (depending on the column length), we studied the possibility of chromatographic analysis of mixtures containing arbitrary concentrations of carbon monoxide. It was established prior to this that carbon monoxide and nitrogen (when present in a gas in high

concentrations) did not separate in columns up to 4.5 m in length.

Table 2 shows several chromatographic analyses of mixtures with high concentrations of carbon monoxide in columns of 4.5, 9, 12, and 15.5 m length. The results of these analyses demonstrated that nitrogen and carbon monoxide separate sufficiently well on a column 9 m long. Mass analyses in a 9-m long column showed that the duration of the analysis, at a carbon dioxide delivery rate of about 20 ml/min, was 30 to 40 min.

We then made analyses with U-shaped columns, about 1 m in length. At this length, the U-columns are convenient to install in the apparatus; in addition, they are easier to fabricate and to fill with adsorbent than spiral columns. A comparison of the analyses in U-shaped and spiral columns showed that 22 - 25 gm activated carbon AG-2 is sufficient for a spiral column with l = 4.5 m and d = = 4.5 - 5 mm whereas a U-shaped column of 1 m length, to separate the components (H_2, N_2, CH_4) just as effectively as a spiral column, must have a diameter of about 12 mm and be filled with 30 - 35 gm of activated carbon AG-2.

Effect of carbon dioxide rate of feed. To define the effect of the rate of carbon dioxide feed on the chromatographic separation of the components, we /2022 performed parallel analyses in spiral columns of 4.5 and 9 m length, at different carbon dioxide feed rates, from 10 to 40 ml/min.

Table 3 gives data on the desorption of pure components at CO_2 flow rates of 15, 20, and 30 ml/min. The experimental results demonstrated that, in these columns, it is more convenient to work with a rate of 20 ml/min. If it is desirable to reduce the analysis time, the separation of hydrogen and nitrogen must be performed at a carbon dioxide flow rate of 15 - 20 ml/min; after separation of the nitrogen, the flow rate of carbon dioxide can be increased to about 60 ml/min. We arrived at this conclusion, based on the following consideration:

At carbon dioxide flow rates of more than 30 ml/min, nitrogen and carbon monoxide are not separated at all in certain mixtures in columns of 4.5 and 9 m length, while high concentrations of nitrogen and hydrogen are difficultly separated in columns of 4.5 m length. A decrease in the flow rate of carbon dioxide

TABLE 2

EXPERIMENTAL RESULTS OF THE CHROMATOGRAPHIC SEPARATION OF GAS MIXTURES OF H_2, N_2, CO, CH_4 IN COLUMNS OF DIFFERENT LENGTH WITH A DIAMETER OF 4.5 mm

Column Length (m)	Component	Time					Flow Rate of CO_2 (ml/min)	Component Content (%)
		t_H	t_K	Δt	h	t_{total}		
4.5	H_2	1min30sec	3min50sec	2min20sec	0min40sec	—	—	27.0
	N_2	4min30sec	0min20sec	4min50sec				15.0
	CO				4min40sec			55.7
	CH_4	14min	16min	3min		16min	20min	2.3
9.0	H_2	2min10sec	6min	3min50sec	3min10sec	—	—	27.0
	N_2	9min10sec	12min30sec	3min20sec	0min20sec	—	—	15.0
	CO	12min50sec	16min	3min10sec		—	—	55.7
	CH_4	27min	32min	5min00sec	11min	32min	20	2.3
9.0	H_2	2min40sec	6min30sec	3min50sec	3min30sec	—	after 14 min increased to 40 ml/min	27.0
	N_2	10min	14min	4min	0min40sec	—		15.0
	CO	14min40sec	16min30sec	1min50sec		—		55.7
	CH_4	22min	24min	2min	3min30sec	24		2.3
12.0	H_2	—	—	—	—	—	—	—
	N_2	14min	18min50sec	4min50sec	0min20sec	—	—	31.5
	CO	19min10sec	24min	4min50sec			—	24.5
	CH_4	36min	48min50sec	7min50sec	12min	48min50sec	20	44.0
15.5	H_2	—	—	—	—	—	—	—
	N_2	19min	23min	4min	1min	—	—	31.5
	CO	24min	32min	8min		—	—	24.5
	CH_4	45min	55min	10min	13min	55min	20	44.0

promotes separation of the components, but leads to an increase in the analysis time and to such blurring of the bandwidth of the low-concentration components in the gas mixture that it becomes difficult to note the start and end of their separation or even the very separation of the components.

Based on experiments as to the effect of column length and flow rate of carbon dioxide on the efficiency of the analysis, we worked out two variants of

chromatographic analysis of gas mixtures with high concentrations of carbon monoxide, at an analysis time of about 20 min.

1. Method of analyzing H_2, N_2, CO and CH_4 with a change in the carbon dioxide flow rate. The analysis was carried out in a column of 9 m length, in the following manner: Before the end of separation of N_2, the components were de-

TABLE 3 /2023

RESULTS OF DESORPTION OF PURE COMPONENTS AT DIFFERENT CARBON DIOXIDE FLOW RATE IN COLUMNS OF 9 AND 4.5 m LENGTH

Component	Separation of Components			Volume of Component (ml/min)	Flow Rate (ml/min)	Column Length (m)
	Start	End	Duration			
H_2	3 min 10 sec	8 min 30 sec	5 min 20 sec	1.5	15	9
N_2	9 min 20 sec	13 min 40 sec	4 min 20 sec	1.4		
CO	14 min	19 min	5 min	1.6		
CH_4	39 min	49 min	10 min	2.3		
H_2	2 min 40 sec	6 min 10 sec	4 min 30 sec	1.5	20	9
N_2	7 min 40 sec	10 min	2 min 20 sec	1.5		
CO	11 min 50 sec	15 min 50 sec	4 min	1.5		
CH_4	26 min 20 sec	32 min 30 sec	6 min 30 sec	2.5		
H_2	2 min 30 sec	5 min	2 min 30 sec	1.1	30	9
N_2	6 min 10 sec	8 min 30 sec	2 min 20 sec	1.6		
CO	6 min 30 sec	10 min	3 min 30 sec	1.7		
CH_4	17 min 40 sec	22 min 40 sec	5 min	2.5		
H_2	1 min 30 sec	4 min 40 sec	3 min 10 sec	2.0	15	4.5
N_2	5 min	10 min 40 sec	5 min 40 sec	2.2		
CO	6 min	12 min 30 sec	6 min 30 sec	2.3		
CH_4	17 min	23 min	6 min	2.5		
H_2	1 min 10 sec	4 min	2 min 50 sec	2.0	20	4.5
N_2	4 min	7 min 10 sec	3 min 10 sec	2.3		
CO	5 min	9 min 10 sec	4 min 10 sec	2.1		
CH_4	12 min	16 min 30 sec	4 min 30 sec	2.5		
H_2	0 min 50 sec	3 min 30 sec	2 min 40 sec	2.0	30	4.5
N_2	2 min 40 sec	5 min 20 sec	2 min 40 sec	2.3		
CO	3 min 50 sec	6 min 50 sec	3 min	2.5		
CH_4	8 min 30 sec	12 min 40 sec	4 min 10 sec	2.5		

veloped at a carbon dioxide flow rate of 20 - 30 ml/min, after which the flow rate of carbon dioxide was increased to above 40 ml/min. When calculating the concentrations it is necessary to take into account the change of the "blank". At a CO content of more than 30%, the flow rate of carbon dioxide at the start

of analysis is best taken as 15 - 20 ml/min, in order to have a sufficient time interval between the separation of nitrogen and carbon monoxide. Mixtures with a CO content less than 15% can be analyzed at a rate of about 40 ml/min during the entire analysis.

2. Analysis with switching of columns. For an analysis with switching of columns in the chromatograph (Fig.1) it is necessary to install, between the stopcocks 6 and 11, two instead of one series-connected columns of 4.5 m length each, with two additional stopcocks (37 and 38). The unit for connecting the columns is shown in Fig.2.

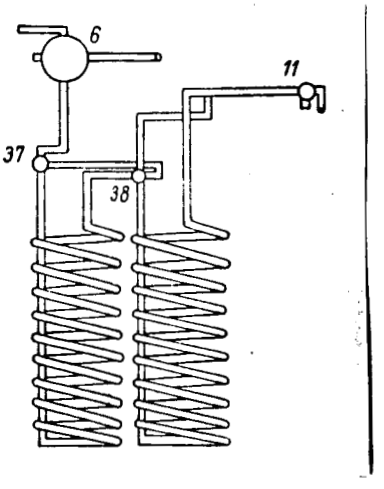

Fig.2 Schematic Diagram of Unit (see Fig.1)

Before performing the main analysis, a preliminary analysis is carried out in one column (the first, with respect to the flow of carbon dioxide) to determine the time interval between the end of CO separation and the start of CH_4 separation. The time interval between separation of CO and CH_4 will vary slightly, depending on the composition of the gas mixture being analyzed. In making mass analyses of mixtures with similar component concentrations, it suffices/2024 to determine the time of switching the columns (making the preliminary analysis),

once for a series of analyses.

The main analysis, with determination of high concentrations of CO, is performed in two series-connected columns in the following manner:

At the start of analysis, the carbon dioxide stream fed to the first column along the flow path of this gas, passes through both columns. Approximately at the middle of the time interval between the end of CO separation and the start

TABLE 4

RESULTS OF CHROMATOGRAPHIC ANALYSES IN TWO U-SHAPED COLUMNS OF MIXTURES RICH IN CO
Composition of Mixture (%): H_2, 25 - 45; N_2, 10 - 20; CO, 40 - 56; CH_4, 0.5 - 6.5

Column Length (m)	Number of Columns	Grade of Carbon	Weight of Carbon (gm)	Flow Rate of CO (ml/min)	Time Interval between Component Separation (min)			Duration of Analysis (min)	Remarks
					H_2—N_2	N_2—CO	CO—CH_4		
2	2	AG-2	62	20	3.5	0.5	10	37 ÷ 40	—
				20	2 ÷ 3	1.6	2 ÷ 2.5	20 ÷ 25	With switching of columns
				—	2.5	0.3	2	20 ÷ 25	After separation of N_2, the feed rate for CO_2 was increased to 35 - 40 ml/min

of CH_4 separation, which is determined in the preliminary analysis, the feed of carbon dioxide to the first column is stopped by closing off this column by turning the stopcocks 37 and 38. When the first column is cut off, methane remains in this column while hydrogen, nitrogen, and carbon monoxide fill the second column and are developed there. After separation of CO, the stopcocks 37 and 38 are turned to cut off the flow of carbon dioxide to the second column and to feed to the first column, for developing the methane.

For illustration, Table 4 gives the results of analyses performed with the method variants described above (data from 5 - 7 analyses).

Effect of sample volume. The accuracy of chromatographic analysis increases with an increase in the sample volume, because of the greater accuracy of detection. This is apparent from the following example: In our buret with scale divisions of 0.01 ml, the percent of absolute error will be calculated by the formula $\delta = \frac{0.01 \cdot 100}{v}$,

where v is the volume of the sample.

The absolute error (at a 0.01 ml error in measuring the volume) calculated by this formula is shown below.

Volume of sample (ml)	1.5	4	10	50
Absolute error (%)	0.7	0.25	0.10	0.02

At the same time, it should be noted that the efficiency of separating components in the chromatographic column may deteriorate with an increase in sample volume. This circumstance limits the possibility of increasing the sample volume.

To define the effect of the sample volume on the efficiency of separating H_2, N_2, CO, CH_4, we determined the starting and end times of discharge of /2025 these components from the chromatographic column, with carbon dioxide development of different volumes of pure components and mixtures of these components having different percentage compositions. Results of these investigations showed that the total duration of analysis of a mixture of H_2, N_2, CO, CH_4 changes little with an increase in sample volume. However, the width μ of the bands of individual components increases with an increase in sample volume and, correspondingly, the time intervals between the separation of adjacent components h decrease; with a further increase in sample volume, the bands of the components are superposed and the components are not separated.

If, for two components that are adjacent with respect to separation, we plot on a graph the curve of t_e versus the volume for the component which separates first and the curve t_s versus the volume for a component which separates next from the mixture (Fig.3), then the point of intersection of these curves

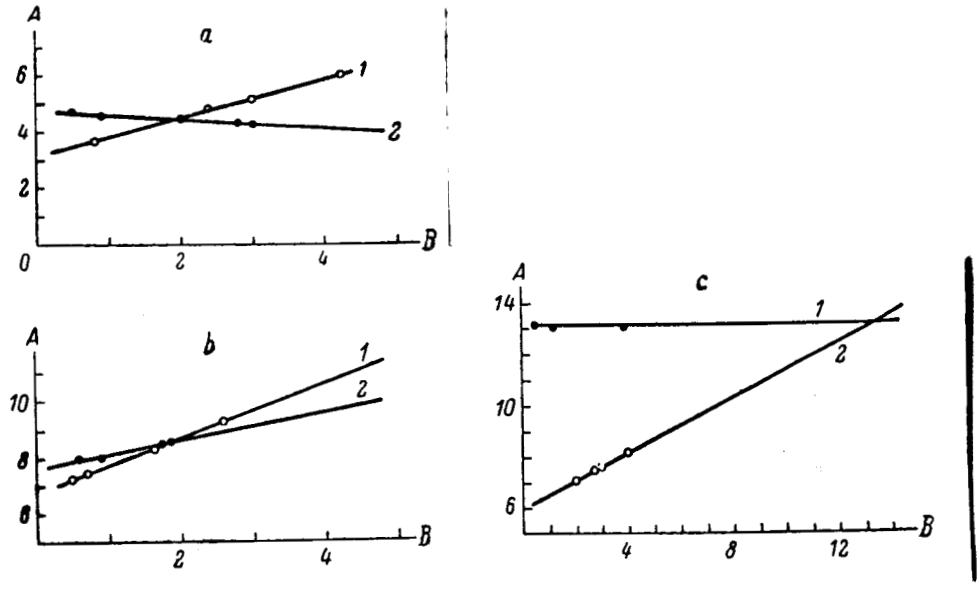

Fig.3 Volume of Components Separated from the Mixture as a Function of Time
A - Time (min); B - Volume of components (mℓ).
a - Column 4.5 m long: 1) t_e - H_2; 2) t_s - N_2.
b - Column 9 m long: 1) t_e - N_2; 2) t_s - CO.
c - Column 4.5 m long: 1) t_s - CH_4; 2) t_e - N_2

will give the volume of these components in the sample, at which their separation is possible. The total volume is equal to the doubled value of the abscissa. The segments between the curves t_e and t_s to the left of their point of intersection represent the time (between separation of components) during which the pure gas carrier is separated at the volume indicated on the abscissa. For example, at a total volume of H_2 and N_2 equal to 2.8 mℓ, the time interval between the end of separation of H_2 and the start of separation of N_2 will be equal to about 30 sec.

These graphs (Fig.3) are convenient for selecting the optimum conditions for making a chromatographic analysis of mixtures of H_2, N_2, CO, and CH_4 of different percentage composition, using this apparatus. It follows from the graphs that the content of hydrogen and nitrogen in the sample, when analyzed in a column of 4.5 m length, should not exceed 4 mℓ. Consequently, at higher concentrations of hydrogen and nitrogen in the analyzed mixture, no more than a 4-mℓ sample should be taken. At high concentrations of methane, the sample can be increased to 20 mℓ. In the case of analyzing mixtures with high CO concentrations, the analysis must be performed in a column of 9 m length, and the sample should not contain CO and N_2 in a total of more than 3.6 mℓ.

BIBLIOGRAPHY

1. Zhukhovitskiy, A.A. and Turkel'taub, N.M.: Gas Chromatography (Gazovaya khromatografiya). Gostopizdat, 1962.
2. Bayer, E.: Gas Chromatography (Khromatografiya gazov). Int. Lit., Moscow, 1961.
3. Shay, T.: Theoretical Principles of Gas Chromatography (Teoreticheskiye osnovy khromatografii gazov). Int. Lit., Moscow, 1963. /2026
4. Turkel'taub, N.M. and Zhukhovitskiy, A.A.: ZL, Vol.31, No.9, p.1026, 1957.
5. Torocheshnikov, N.S. and Semenova, V.A.: Vestn. tekhniko-ekonom. inform., Vol.10, p.55, 1960.
6. Torocheshnikov, N.S. and Semenova, V.A.: Zh.Prikl.Khim., Vol.33, p.597, 1960.
7. Kotlik, B.Ye. and Budol', Z.P.: Koks i khimiya, Vol.8, p.31, 1962.
8. Torocheshnikov, N.S. and Semenova, V.A.: Method of Analyzing Combustible Gas Mixtures (Metodika analiza goryuchikh gazovykh smesey). MKhTI im. D.I.Mendeleyeva, 1965.